PILOT PLANT STUDY OF MERCURY CONTROL IN FLUE GAS FROM COAL-FIRED BOILERS

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BACKGROUND

Mercury control technology options for coal-fired boilers are ill-defined. Commercial development of mercury emissions control technologies has centered on high concentrations of mercury compared to the levels present in the flue gas from coal combustion, typically 5 to 10 $\mu g/m^3$. In addition, most mercury in these commercial applications (medical waste and municipal solid waste incinerators)[1,2,10] is in the form of $HgCl_2$; flue gas from coal-fired units contains both ionic and elemental mercury. Reaction mechanisms may be different for these two species. Development work at the lower concentrations has centered on small scale, fixed-bed, laboratory studies.[8,9,12] Recent tests at coal combustion sources with sorbents such as lime[3,5,7] and activated carbon[4] have shown some mercury removal. However, neither the laboratory nor combustion tests completely address process design issues. In the laboratory studies, the actual process conditions are very different from those with coal; while in the combustion tests, it is difficult to vary the conditions. In addition, data reliability is poor because of the difficulty of mercury sampling and analysis.

Development of mercury control technology for coal-fired flue gas requires:

1. Accurate and reliable sampling and analytical techniques, including speciation of mercury,

2. A thorough understanding of the effects of the combustion conditions and of the speciation of mercury on mercury removal,

3. Identification of sorbents and process configurations for removal of mercury at the low levels present in coal-fired flue gas, and

4. Waste management studies and economic evaluation of control technologies.

Each of these factors is important in developing a process to control mercury emissions. To this end, a 0.2 MWe equivalent, continuous flow pilot plant was constructed at CONSOL R&D to evaluate the efficiency and cost of sorbent injection technology for mercury control, and to verify mercury sampling and analysis techniques.

DESCRIPTION OF THE FACILITY

The 0.22 Nm^3/s (500 scfm) pilot plant is of sufficient size to provide a realistic process simulation while maintaining the capability to study the effect of potentially important variables such as sorbent/flue gas residence time, fly ash loading, and mass transport phenomena. It provides accurate and independent control of key process variables, including mercury concentration and speciation. The flue gas mercury concentration can be varied between 2 and 20 $\mu g/m^3$, a range typical of coal combustion. By adding actual coal fly ash, the physical and chemical fly ash/ sorbent interactions are realistically simulated. Because the pilot plant is a flow system, the mass transfer conditions, temperature/time history, and gas/solid interactions can be varied to simulate conditions in a coal-fired power plant.

The sorbent injection pilot plant accurately simulates flue gas downstream of the air preheater in a coal-fired boiler. The plant was designed to simulate a wide range of site-specific conditions by burning natural gas and by injecting the deficient components such as fly ash, CO_2, SO_2 and mercury compounds. Independent control of the temperature (38-205 °C, 100-400 °F), humidity, sorbent injection and sorbent recycle rate is maintained. The pilot plant was proven to be a reliable, accurate tool for desulfurization studies when its results for the Coolside process were scaled up to a 105 MWe demonstration at the Ohio Edison Edgewater plant.[13]

Figure 1 is a schematic of the 0.22 Nm^3/s (500) scfm sorbent injection pilot plant. Originally used in the development of the Coolside and Advanced Coolside desulfurization processes,[15] it was modified for mercury control studies. The plant consists of a flue gas generation system, a flue gas conditioner for temperature and humidity control, a mercury spiking system, fly ash and sorbent injection systems, a sorbent recycle system, flue gas duct work, particulate removal systems (cyclones and a baghouse), a waste handling system, and flue gas

analysis systems. The pilot plant provides accurate and independent control of flue gas temperature and composition. Accurate control of mercury concentration and speciation in the simulated flue gas is maintained independently of the bulk flue gas composition. The feed and effluent sorbent streams and flue gas stream can be sampled. The pilot plant is instrumented and automated for process control and data collection. A natural gas combustor, a steam injection system and the flue gas conditioner are used to control flue gas humidity and temperature independently. Control loops on these systems allow flue gas temperature to be maintained automatically between 38 and 205 °C within ±0.5 °C (100 and 400 °F within ±1 °F) and the approach to adiabatic saturation to be controlled within ±0.5 °C (±1 °F).

The feed system for elemental mercury consists of mercury-containing permeation tubes, a constant temperature bath and an inert carrier gas. The tubes are commercially available, and are an accurate, reproducible method for feeding mercury. The temperature of the tubes is controlled to within ±0.01 °C (±0.02 °F) by a constant temperature bath. The permeation rate for the tubes is calibrated by weighing the tubes over a known period. In long-term tests, weight loss of the tubes is used to verify the mercury material balance. Mercuric chloride is fed by a separate, similar subsystem. Similar calibrations were carried out on the $HgCl_2$ feed system. By adding Hg^0 and $HgCl_2$ to the flue gas independently, the amount and speciation of mercury are controlled to within 5%.

The solids are collected using a cyclone or a baghouse. The sorbent collected by the cyclone is almost instantaneously removed from contact with the flue gas stream. This allows solids to be collected after a short, well-controlled contact time with the flue gas (1-3 sec). With two parallel particulate collecting devices, in-duct removal can be measured separately from baghouse removal. The in-duct mercury removal allows estimation of the Hg removal in an ESP-equipped unit.

Recycling the flue gas reduces reagent costs and assists in maintaining a consistent flue gas composition. A large fixed-bed carbon filter prevents recycle of Hg^0 or $HgCl_2$ not removed by the sorbent.

For all the flue gas sampling tests, the simulated flue gas contained 1000 ppmv SO_2, 10% O_2, and 10% CO_2, and had a saturation temperature of 52 °C (125 °F). The flue gas flow was accurately controlled and monitored with a thermal dispersion mass flowmeter, and checked by standard manual procedures (pitot tube/differential pressure gauge). The gas sampling was conducted in a section of the pilot plant duct located approximately 16.8 m (55 ft) downstream of the mercury injection point. There are a gas distribution plate in the duct just downstream of the injection point and several direction changes of the flue gas (90° bends) prior to sampling to distribute mercury in the flue gas.

TEST PROGRAM

Initial Operations

Verification and, if necessary, improvement of sampling/analytical techniques is the first task in the experimental program. Accuracy and reliability are critical for measuring flue gas mercury concentration, for determining speciation, to provide reliable data for process development, and for scale-up to commercial application. Because the mercury concentration and speciation are accurately controlled in the pilot plant, any error in the sampling/analytical methods can be determined.

Sorbent Evaluation/Development

Identification of an inexpensive, effective sorbent is a primary objective of this work. Understanding the effects of temperature, humidity and mercury speciation on sorbent performance is critical for designing a viable process. To achieve this, statistically designed screening tests will be performed on each candidate sorbent. For candidate sorbents, significant process variables will be explored in more detail. Steady-state tests, with sorbent recycle, will be made with the most cost-effective sorbents. These runs will last two to three days, until steady-state conditions are demonstrated by solid analysis.

Waste Management Studies

Several important technical issues involve waste management. These include mercury leaching, revolatilization and the impact of mercury on ash utilization. However, utilization of solid waste is preferable to disposal and can accelerate commercialization. The program will evaluate options for waste utilization, with emphasis on the high volume use of the material in construction. A successful approach to eliminate or reduce the need for waste disposal represents a substantial improvement in the state of sorbent injection processes.

Economics

Engineering and economic studies will be conducted to determine the feasibility of process operations. Sorbent injection processes have inherently low capital costs; therefore, sorbent cost is a key issue. Hydrated lime may be effective

for removing some ionic mercury and is low in cost; however it may not be effective in removing elemental Hg. High surface area activated carbons are expensive ($0.50-0.80/kg ($450-1000/ton)), and chemically impregnated sorbents are even more expensive by a factor of five. The minimum amount of sorbent required is not known and likely will vary among applications. The potential of recycle to increase sorbent utilization also will be addressed. Integration of mercury control with other flue gas treatment systems represents a significant improvement in the process economics. Process economic studies also will allow research to focus on areas of the most potential benefit to process economics.

INITIAL RESULTS

Mercury Feed System

Calibration of the elemental mercury (Hg^0) and mercuric chloride ($HgCl_2$) feed system showed a high degree of accuracy and precision. In replicate tests of weight loss vs time, the variation from the amount of Hg^0 or $HgCl_2$ fed at a particular calibration condition was ±4% or less for Hg^0 and ±5% for $HgCl_2$. Figure 2 shows the Hg^0 calibration data. In these tests, the weight loss of several of the commercially available Hg^0 permeation tubes was measured as a function of temperature. In these calibration tests, emphasis was placed on 110 and 114 °C, the typical temperatures of the Hg^0 feed system pilot plant operations. Six calibration runs were made at each of these two temperatures. Similar precision was obtained in the calibration of the $HgCl_2$ feed subsystem. Figure 3 shows the amount of $HgCl_2$ evolved at three different calibration conditions. The data represent four to six replicate tests at each calibration condition.

Flue Gas Sampling and Analysis

Several preliminary tests were made in which Hg^0 and/or $HgCl_2$ were added to the pilot plant flue gas, and the gas sampled using EPA Method 29, followed by cold vapor atomic absorption (CVAA) analysis of the impingers solutions.[14] The flue-gas mercury concentration in these tests was 4 to 24 $\mu g/m^3$, typical of concentrations found downstream of a coal-fired boiler. Figure 4 shows that in tests with only Hg^0 addition, there was very good agreement between the Method 29 gas sampling/analysis results and the amount of Hg^0 fed to the flue gas via the feed system. The mercury concentration in the flue gas based on Method 29 results was 10 to 12.5 $\mu g/m^3$, compared to 9 to 9.5 $\mu g/m^3$ based on feed system calibration. In the $HgCl_2$ tests, the flue gas mercury concentration based on sampling/analysis was, on average, 30% lower than that based on the feed system calibration (Figure 4 and Table 1). It appears that the ionic mercury present in the pilot plant flue gas was not entirely recovered and/or detected by the Method 29 sampling train and analytical procedures. The accuracy of the mercury feed rates were further confirmed by injecting a large excess of activated carbon at low temperature (<93 °C or 200 °F), and measuring the mercury captured by analysis of the sorbent recovered from the baghouse.

Table 1 shows that the ionic mercury ($HgCl_2$) was in general evenly distributed between the front impingers containing nitric acid and peroxide and the back set of impingers containing permanganate and sulfuric acid. This was true in several tests in which the mercury concentration in the flue gas was varied. These results are contrary to reported assumptions that ionic mercury is primarily captured in the front impingers.[4,6,11] All the elemental mercury was captured in the back set of impingers (permanganate), which agrees with reported assumptions.[4,6,11] Additional testing will be done to further investigate mercury capture and speciation by Method 29.

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TABLE 1. CAPTURE OF ELEMENTAL AND IONIC MERCURY IN METHOD 29 SAMPLING TRAIN

Test	Species Fed	Mercury Recovered in Impingers, % of Total Mercury Fed	
		HNO_3/H_2O_2	$KMnO_4/H_2SO_4$
A	$HgCl_2$	48	39
B	$HgCl_2$	34	42
C	$HgCl_2$	38	24
D	$HgCl_2$	10	31
E	$HgCl_2$	38	29
F	Hg^0	<4	134
G	Hg^0	<4	106

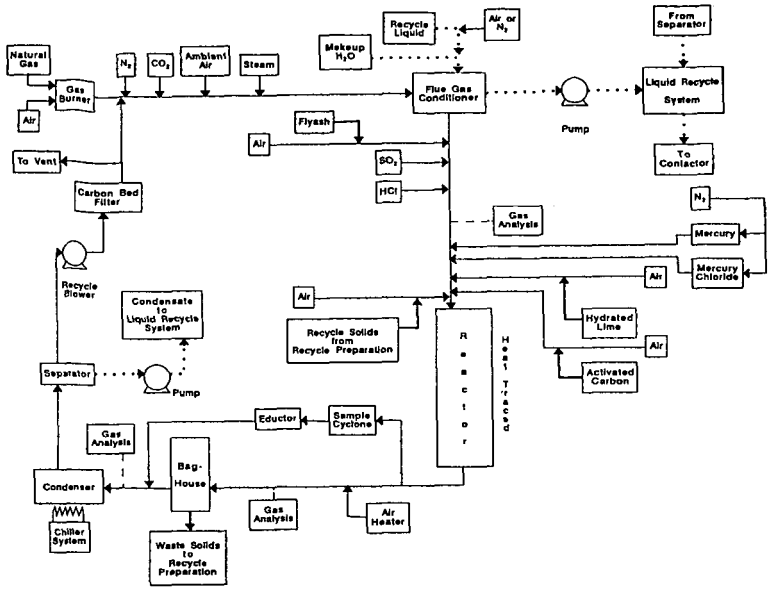

Figure 1. Schematic of CONSOL Sorbent Injection Pilot Plant

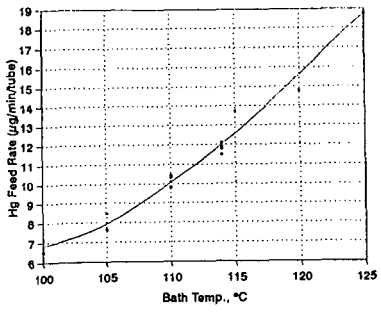

Figure 2. Calibration of Elemental Mercury Feed System.

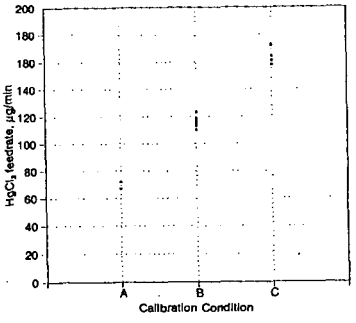

Figure 3. Calibration of Mercuric Chloride Feed System.

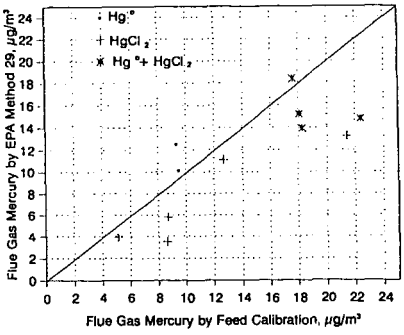

Figure 4. Comparison of Flue Gas Mercury Concentration Based on Method 29, with Concentration Based on Mercury Feed System Calibration.